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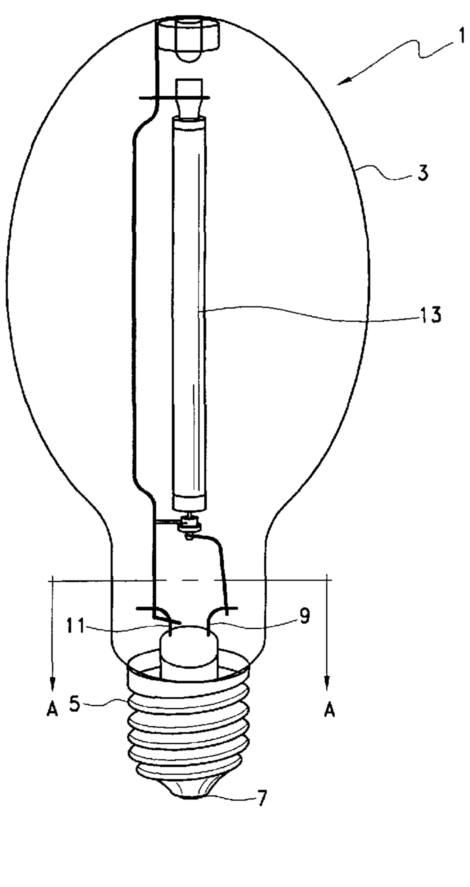
(54) **Title:** NOVEL HIGH-TEMPERATURE LAED-FREE SOLDERS



(57) Abstract: Novel lead-free solder alloys and intermetallic compounds are disclosed. The solders may be used for high intensity discharge lamp (1). Solder joints formed from these alloys are resistant to creep in high-temperature environments such as those experienced by high intensity discharge lamps (1). The lead-free solder alloys.can be reacted with higher melting point additives by a transient liquid phase reaction to form intermetallic compounds which have a melting point higher than that of the lead-free solder alloy.

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TITLE OF THE INVENTION

Novel High-Temperature Lead-Free Solders

TECHNICAL FIELD

The present invention relates to lead-free solder alloys and solder alloy compositions which are particularly useful in lighting applications.

BACKGROUND ART

Pb-Sn alloy solders have been used routinely to join materials. There are many historical reasons for the widespread use of Pb-Sn alloy solders. These reasons include the low solidus temperature of Pb solder alloys, the workability of Pb alloy solders over a wide temperature range, ready availability of process equipment, as well as the low cost of adjuncts such as resins, fluxes, and solder masks. However, lead is a toxic, heavy metal with a relatively high vapor pressure. Its use is disfavored, and a need exists for a replacement.

Several forces are acting to move to more environmentally friendly solders due to health concerns surrounding possible worker contamination, problems with recycling of electronic components, as well as environmental concerns from inadvertent land-fill. Societal efforts have resulted in efforts to remove lead from electronics, paint, food packaging, automobile fuel, and plumbing. Solder now also has been identified as another material to be made free of lead.

Various lead-free solder alloys are known. U.S. Pat. Nos. 4,643,875 and 4,667,871 describe high temperature brazing alloys containing from 35% to 95% Sn, from 0.5 to 70% Ag, from 0.5 to 20% Cu, effective amounts of one or more of Ti, V, and Zr, and optionally with Ni, and Cr. The disclosed brazing alloys require temperatures of at least 550 °C for good bonding.

U.S. Pat. No. 4,778,733 describes an article of manufacture containing from 92 to 99% Sn, from 0.7 to 6% Cu,

and from 0.05-3% Ag.

U.S. Pat. No. 4,797,328 describes soft-solder alloys for bonding ceramic parts without premetallization. The alloys, which are disclosed to be useful for bonding alumina parts to Cu parts, contain from 86 to 99% Sn, from 0 to 13% Ag and/or Cu, from 0 to 10% In, and from 1 to 10% Ti.

U.S. Pat. No. 4,806,309 describes solder alloys containing from 90 to 95% Sn, from 3 to 5% Sb, from 1 to 4.5% Bi, and from 0.1 to 0.5% Ag.

A primary application for Pb-Sn alloy solder is in electronic assembly. Accordingly, most Pb-free solder alloys considered for use as a replacement for Pb-Sn alloy solders seek to have physical properties similar to Pb-Sn solder alloys. Pb-Sn solder alloys, however, are undesirable due to environmental concerns.

Materials of ruse in lighting applications must be able to withstand temperatures in excess of about 200°C for time periods in excess of about 20,000 hours. Pb-Sn alloys, in addition to environmental concerns, suffer remelting and creep when exposed to the high operating temperatures of high intensity discharge lamps for extended time periods. High intensity discharge lamps require solders which survive high operating temperatures of more than 200 °C for extended time periods of approximately 2000 hours.

In manufacture of devices such as high intensity discharge lamps, it is desirable to use low solder melting temperatures to reduce heating time and to facilitate rapid assembly. The solder alloys, however, should not remelt and creep at the operating temperatures of the lamp.

A need therefore exists for lead-free solder materials which avoid the remelting and creep problems of the solders of the prior art.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a front view of an improved high intensity discharge lamp.

FIG. 1A is an enlarged, partial cross-sectional view taken along section line A-A of FIG. 1.

FIG. 2 represents a side view of an alternative embodiment of the high intensity discharge lamps shown in FIG. 1 where the base is at a right angle to the light source.

FIG. 2A is a side view of FIG. 2 showing lead wires.

FIG. 2B is a cross sectional view taken on line BB of FIG. 2.

FIG. 2C is an end view taken in the direction of Arrow A.

FIG. 3 is a side view in partial cutaway cross section of an improved sealed beam lamp.

FIG. 3A is a cross sectional view of FIG. 3 taken on line AA.

FIG. 4 is a side view of an improved composite lamp.

FIG. 4A is a cross sectional view of FIG. 6 taken on line AA.

FIG. 4B is a bottom view of the base section of the lamp of FIG. 4 taken in direction of arrow B.

FIG. 5 is a side view of an improved flourescent lamp.

FIG. 5A is an enlarged view of the plug section of the flourescent lamp of FIG. 5.

DISCLOSURE OF THE INVENTION

In a first embodiment, the invention relates to lead-free solder alloy compositions and lead-free solder alloys formed from those compositions. The solder alloys have melting characteristics favorable for use in lighting applications such as high intensity discharge lamps, sealed beam lamps, and composite lamps. More particularly, the invention relates to a lead-free solder alloy of Sn, Bi and Sb wherein Sn is present in an amount of about 45 wt.%, Bi is present in an amount of about 20 wt.%, and Sb is present in an amount of about 33

wt.%, all amounts based on the total weight of the alloy.

In another aspect, the invention relates to a lead-free solder alloy of Sn, Sb, and Cu wherein Sn is present in an amount of about 71 wt.%, Sb is present in an amount of about 24 wt.%, and Cu is present in an amount of about 5 wt.%, all amounts based on the total weight of the alloy.

In a further aspect, the invention relates to a lead-free solder alloy of Sn, Sb and Cu wherein Sn is present in an amount of about 94 wt.%, Sb is present in an amount of about 5 wt.%, and Cu is present in an amount of about 1 wt.%, all amounts based on the total weight of the alloy.

In yet a further aspect, the invention relates to a lead-free solder alloy of Sn, Cu and Ag wherein Sn is present in an amount of about 73 wt.%, Cu is present in an amount of about 2 wt.%, and Ag is present in an amount of about 25 wt.%, all amounts based on the total weight of the alloy.

In a second embodiment, the invention relates to novel compositions of a lead-free solder alloy component and a higher melting point additive component. The additive component can be obtained from, for example, the substrate being soldered or by physical addition of various forms of the additive. The additive component reacts with the molten lead-free solder alloy during soldering to produce a high melting point intermetallic compound which has characteristics favorable for use in lighting applications such as high intensity discharge lamps.

In one aspect, wherein all amounts are in wt.% unless otherwise specified, the invention relates to a high melting point intermetallic compound that includes a reaction product of 20Bi-33Sb-47Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy. In a second aspect, the invention relates to a high melting point intermetallic compound that includes a reaction product of 5Cu-24Sb-71Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy. In another aspect, the invention relates to

a high melting point intermetallic compound that includes a reaction product of 2Cu-25Ag-73Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy. In a further aspect, the invention relates to a high melting point intermetallic compound that includes high melting point intermetallic compound of a reaction product of 1Cu-5Sb-94Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy.

In yet another aspect, the invention relates to a high melting point intermetallic compound that is a reaction product of 20Bi-33Sb-47Sn solder alloy and Cu in an amount of 2.0% based on weight of the solder alloy. In an additional aspect, the invention relates to a high melting point intermetallic compound that includes a reaction product of 20Bi-33Sb-47Sn solder alloy and Cu in an amount of 5.0% based on weight of the solder alloy.

A method of manufacture of a high melting point intermetallic compounds also is disclosed. The method entails reacting a lead-free, solder alloy which includes one or more low melting point component metals such as Sn, Ga and In with an additive which has a melting point greater than the melting point of the lead-free, solder alloy, wherein at least one of Sn, Ga and In is present. At least one of Sn, Ga and In is present in a sufficient amount whereby about 15 to about 50 at.% of the metal is free for reaction with a high melting point additive, based on the total at.% of the lead-free, solder alloy and high melting point additive.

In a preferred aspect, the method of manufacture of a high melting point intermetallic compound entails reacting a lead-free, solder alloy which includes one or more low melting point metals such as Sn, Ga and In with a higher melting point additive such as Co, Ni, Pd, Fe, Cu, Ag, Ti, and Au. At least one of these higher melting point additive metals is present in a sufficient amount whereby about 15 to about 50 at.% of the metal based on the total at.% of the alloy and high

melting point additive, is free for reaction with the high melting point additive.

The invention further relates to an improved high intensity discharge lamp which includes soldered joints such as soldered side joints, soldered eyelet joints and soldered mechanical interlocks which include a solder alloy of any of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn.

The invention also relates to an improved high intensity discharge lamp which includes soldered joints such as soldered side joints, soldered eyelet joints and soldered mechanical interlocks which include an intermetallic reaction product of any of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn solder alloys, and intermetallic reaction products formed of any of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn, and 1Cu-5Sb-94Sn with a high melting point additive such as Cu and Ti.

The invention further relates to an improved sealed beam lamps which includes soldered joints such as soldered side joints, soldered eyelet joints and soldered mechanical interlocks which include an intermetallic reaction product of any of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn, and 1Cu-5Sb-94Sn with a high melting point additive such as Cu and Ti.

The lead-free solder alloys of the first embodiment, as well as the intermetallic compounds formed from reaction of lead-free, solder alloy and high melting point additive metal, have advantages such as electrical conductivity, resistance to long term failure by creep, oxidation, and thermal fatigue, are able to sustain modest stresses in use and during installation, and can be easily repaired.

The compositions used in manufacture of the high melting point intermetallic compounds can be formulated to produce intermetallic products which readily bond to substrates such as Ni plated Fe, Ni alloys such as monel, brass (Cu-Zn) alloys such as 95 wt.% Cu-5 wt.% Zn, and Ni plated Cu-Zn alloys. The high melting point intermetallic compounds have a solidus

temperature of more than about 250°C.

Having summarized the invention, the invention will now be described in detail below by reference to the following detailed description and non-limiting examples.

MODES FOR CARRYING OUT THE INVENTION

In a first embodiment, the invention relates to lead-free solder compositions for manufacture of lead-free solder alloys, and to the lead-free solder alloys produced from those compositions. Although the solder alloys are preferably completely free of Pb, it is to be understood that impurities such as Pb, Cd, and Hg may be present in the lead-free solder alloys in amounts of up to about 0.5% based on the weight of the solder alloy.

In a first aspect of this first embodiment, the lead-free solder alloy compositions relate to component metal compositions for manufacture of lead-free, Sn-Bi-Sb solder alloys, and to Sn-Bi-Sb solder alloys produced from those compositions. In these Sn-Bi-Sb compositions, Sn may be present in an amount of about 30 to about 70 wt.%, preferably about 30 wt.% up to about 40 wt.%, more preferably about 32 wt.%; Bi may be present in an amount of about 1 wt.% to about 45 wt.%, preferably about 20 wt.% to about 45 wt.%, more preferably about 43 wt.%; and Sb may be present in an amount of about 25 to about 35 wt.%, preferably about 25 wt.% to about 30 wt.%, more preferably about 25 wt.%, all amounts based on the total weight of the composition. An especially preferred Sn-Bi-Sb component metal composition has about 32 wt.%Sn, about 43 wt.% Bi, and about 25 wt.% Sb. The lead-free solder alloy produced from this composition is 47Sn-20Bi-33Sb.

In a second aspect of this first embodiment, the lead-free solder alloy compositions relate to component metal compositions for manufacture of lead-free Sn-Sb-Cu solder alloys. In these compositions, Sn may be present in amounts of about 60 wt.% to about 94 wt.%, preferably about 60 to about

88 wt.%; more preferably, about 60 wt.%; Sb may be present in amounts of about 5 to about 30 wt.%, preferably about 10 wt.% to about 30 wt.%, more preferably about 28 wt.%; and Cu may be present in the amounts of about 1 wt.% to about 15 wt.%, preferably about 5 wt.% to about 12 wt.%, more preferably about 12 wt.%, all amounts based on the total weight of the Sn-Sb-Cu component metal composition. An especially preferred component metal composition includes about 60 wt.% Sn, about 28 wt.% Sb, and about 12 wt.% Cu. This composition yields a lead-free solder alloy of 71Sn-24Sb-5Cu. Another especially preferred component metal composition includes about 88 wt.% Sn, about 10 wt.% Sb, and about 2 wt.% Cu. This composition yields a lead-free solder alloy of 94Sn-5Sb-1Cu.

In a third aspect of this first embodiment, the lead-free solder alloy compositions relate to component metal compositions for manufacture of lead-free, Sn-Ag-Cu solder alloys. In these compositions, Sn may be present in an amount of about 55 wt.% to 85 wt.%, preferably about 55 wt.% to about 70 wt.%, more preferably about 58 wt.%; Ag may be present in amounts of about 20 wt.% to about 30 wt.%, preferably about 23 wt.% to about 29 wt.%, more preferably about 26 wt.%, and Cu may be present in amounts of about 1 wt.% to about 18 wt.%, preferably about 10 wt.% to about 16 wt.%, more preferably about 16 wt.%, all amounts based on the total weight of the component metal composition. An especially preferred component metal composition has about 58 wt.% Sn, about 26 wt.% Ag, and about 16 wt.% Cu. This composition yields a lead-free solder alloy of 73Sn-25Ag-2Cu.

Production of Lead-Free Solder Alloys

In manufacture of lead-free solder alloys, the metal components of the alloy are blended, and then furnace melted to form a molten blend. The molten blend then is gas atomized into powder. The component metals employed are in the form of shot of about 99.5% purity. Shot of Sn, Zn, Sb and Cu are

obtained from Nathan Trotter, Inc. Bi and Ag shot are obtained from Alpha-Fry Technologies, Altoona, PA.

Furnace melting is done at temperatures sufficient to achieve homogenization, preferably complete homogenization, of the alloy formed from the metals. Homogenization is performed at temperatures below that which would undesirably cause one or more of the component metals to vaporize so as to produce a solder alloy that deviates from the desired solder alloy.

Homogenization is achieved when the melt is held at a sufficient temperature for a sufficient time to produce a homogenous molten alloy, that is, an alloy which is free of chemical gradients over a thickness of about 1 mm. If in the event that vaporization of a component metal such as Sb, Cu, Zn, Bi occurs so as to produce a solder alloy which deviates from the desired solder alloy, loss of the component metal can be compensated by including an additional amount of that component metal in the melt.

In a preferred aspect of manufacture of lead-free solder alloys, the component metals are mixed in a tapered cylindrical alumina crucible, and heated in a retort furnace equipped with an Inconel shell in dry hydrogen that has a dew point of -40°C or less to produce a homogenous alloy. The heating program employed to produce a homogenous solder alloy entails heating the component metal compositions at about 5°C/min to the melt temperature, holding the resulting melt for about 3 hours to achieve homogenization, and then furnace cooling at about 10°C/min to room temperature to form a slug of homogenous, lead-free solder alloy. This heating program may be varied according the specific component metal composition. Accordingly, the crucible material and shape, use of faster or slower heating rates, use of faster or slower cooling rates, use of differing soak temperatures and time periods may be varied.

In order to produce atomized powders of lead-free solder alloys, slugs of the lead-free solder alloy produced above are

cut by a 25 cm resin-bonded alumina abrasive cut off wheel into 12 mm x 12 mm x 25 mm pieces. These pieces are placed into the melt crucible of a model Atomatic Lab-scale gas atomizer from HJE Corp., Glen Falls, NY. Graphite is the preferred material for the melt crucible. The crucible may, however, be formed from any material compatible with the heating system of the atomizer and which does not react with the molten alloy. Examples of other materials which may be used as a crucible include alumina, silica, mullite, glasses, zirconia, stainless steel and high-chrome steel.

The solder alloy pieces, after having been placed into the atomizer, are induction heated under argon by using an Inductotherm VIP Power-Trak induction power supply connected to a water-cooled induction coil. The solder alloy pieces are superheated to above their theoretical liquidus, preferably about 150 ^{0}C above their theoretical liquidus. The molten, superheated solder alloys are then atomized by the atomizer at a nitrogen gas pressure of about 1.1 MPa.

During atomization, molten solder alloy is drawn by the gas pressure through a graphite nozzle of 2.5 mm diameter. The pressures and nozzle size conditions are sufficient to produce an atomized powder which has a particle size range of about 10µm to about 250 µm. The atomized powder is sieved to remove particles and agglomerates larger than 90 µm. The diameters of the nozzle, melting conditions, atomization temperatures, and atomization gas pressures can be varied to produce powders of a desired range of particle size and shape. Accordingly, inert gases other than argon such as nitrogen and helium may be used as the cover gas for the melt while in the melt crucible and as the atomization gas. Hydrogen or air also can be used as a cover gas for the melt depending on the composition of the solder alloy and process equipment.

The invention will now be described by reference to the following non-limiting examples.

Examples 1-8:

Using the procedure described above, the component metal compositions of examples 1-8 of Table 1 are melted, homogenized, and then atomized into powder of lead-free solder alloy. The component metal compositions employed, the melt and homogenization temperatures used, as well as the atomization temperatures and pressures used are given in Table 1. In Table 1, the wt.% amounts of the component metals used in the component metal composition are based on the total weight of the component metal composition.

The lead-free solder alloys produced from the component metal compositions also are shown in Table 1. Differences in composition between the solder alloy produced and the component metal composition is due to volatilization of one or more of the metal components used in the component metal composition.

The solder alloys of Table 1 are analyzed by electron microprobe and inductively coupled plasma mass spectroscopy. In Table 1, the wt.% amounts of the metals in the resulting lead-free solder alloy are based on the total weight of the solder alloy.

Table 1

Ex.	Component Metal Composition (wt.%)	Homogenization Temp. (°C)	Melt Temp. (°C)	Atomization Temp. (°C)	Atomization Pres. (MPa)	Solder Alloy (wt.%)
1	13Sn-80Bi-7Sb	600	600	400	1.2	**
2	74Sn-16 Bi-10 Sb	600	700	500	1.2	**
3	32Sn-43Bi-25Sb	600	660	500	1.1-1.2	20Bi-33Sb-47Sn
4	41Sn-36Bi-23Zn	600	550	450	0.9-1.2	**
5	44Sn- 46Bi-10Zn	600	500	400	1.0-1.2	**
6	60Sn-28Sb-12Cu	800	600	580	1.2	5Cu-24Sb-71Sn
7	58Sn-16Cu-26Ag	800	650	650	1.0-1.1	2Cu-25Ag-73Sn
8	88Sn-10Sb-2Cu	800	450	450	1.1-1.3	1Cu-5Sb-94Sn

**. Not analyzed

The solidus and liquidus temperatures of the lead-free solder alloys in Table I are measured using a Netzsch STA 409 Differential Scanning Calorimeter (DSC)under argon. The thermal profile used entails heating atomized lead-free solder alloy powders at 10^{0}C/min to either 500^{0}C or to 600 ^{0}C, and then cooling at 10^{0}C/min to a temperature of 50^{0}C. This cycle is repeated twice to determine the solidus and liquidus on initial heating, and after full melting and re-solidification. The first cycle simulates initial melting of the solder alloy during soldering. The second cycle simulates the solder alloy properties after the solder joint has been formed.

The solidus and liquidus temperatures for the lead-free solder alloys of Table 1 are given in Table 2.

Table 2

Solder Alloy Of Example #:	First Cycle Solidus (°C)	First Cycle Liquidus (°C)	Second Cycle Solidus (°C)	Second Cycle Liquidus (°C)
1	195	225	134	223
2	188	378	138	355
3	138	354	138	354
4	129	343	126	349
5	128	272	125	172
6	231	415	232	400
7	210	430	210	485
8	231	267	231	265

High Melting Point Intermetallic Compounds

In this embodiment, mixtures which include one or more lead-free solder alloys and one or more high melting point additive metals which have a melting point higher than the lead-free solder alloy are reacted to produce a high melting intermetallic compound. The intermetallic compound has a melting point higher than that of the lead-free solder alloy.

The lead-free solder alloy employed includes one or more component metals such as Sn, Ga and In which can form intermetallic compounds with the high melting point additive metals at the soldering temperature. Typically, the amount of Sn in the lead-free solder alloy is more than about 45 wt.% based on the weight of the solder alloy, preferably more than about 60 wt.%, more preferably more than about 85 wt.% Sn. The Sn content in the solder alloy, however, is not so high as to cause corrosive attack of the substrate by the solder alloy over long-term exposure of the substrate to temperatures above about 200°C.

Examples of useful lead-free solder alloys which have Sn as the low melting point component metal have about 15 at.% to about 50 at.% free Sn. Free Sn is Sn which is not strongly bound within the lead-free solder alloy and which is able to react with the additive metals. Where the low melting point metal in the lead-free solder alloy is In or Ga, useful lead-free solder alloys typically have about 15 at.% to about 50 at.% free In or Ga. Especially preferred lead-free solder alloys include the alloys of examples 3,6,7 and 8 of Table 1. These lead-free solder alloys have high solubility for the high melting point additive metals.

The high melting point additive metals may be employed in various forms with the lead-free solder alloys. These high melting point additive metals include but are not limited to transition metals such as Co, Ni, Pd, Fe, Cu, Ag, Ti, and Au; alloys of transition metals such as Cu-based alloys such as brass and bronze; Ni-Cu alloys such as monel; Ni-Fe alloys such as Invar; Pd alloys such as Paliney alloys; Ti alloys such as Ti-6Al-4V; Co alloys such as Vitalium and other Co-Cr alloys; precious metal alloys such as sterling silver, gold, gold-palladium alloys, and gold-silver alloys, ferrous alloys such as low-alloy steel, and alloys of other metals such as Kolar (Fe-29Ni-17Co).

The high melting point additive metals may be obtained from various sources in forms such as powder, wire, and ribbon. The high melting point additive metals also may be obtained by diffusion from the substrate when the substrate is heated during soldering. In this aspect, care must be taken that the solder alloy does not react so strongly with the substrate that it penetrates or otherwise adversely affects the substrate.

The amount of high melting point additive metal provided by diffusion from the substrate can be controlled by varying the time and/or temperatures employed during the soldering process. The amount of high melting point additive metal diffused from the substrate also can be controlled by varying the surface area of the high melting point additive metal. For example, a lead-free solder alloy in the form of a thin wire which has a high surface area compared to the substrate is contacted with the substrate. By increasing the surface area of the solder alloy, the amount of high melting point additive metal diffused from the substrate during soldering increases; similarly, decreasing the surface area decreases the amount of high melting point additive metal diffused during soldering.

In order to maximize the effectiveness of the high melting point additive metal for reaction with the lead-free solder alloy to form a high melting point intermetallic compound, the presence of undesirable low melting point metals which may reduce solubility of the high melting point additive metal in the molten lead-free solder alloy is minimized. Examples of these undesirable metals include Zn, Bi, Cs, Cd, Hg, and Ga.

The atomic ratios of any of these undesirable metals to the intermetallic-forming component of the solder typically is less than about 0.3, based on the total atomic composition of the lead-free solder alloy. For example, in lead-free solder alloys where Sn is the predominant intermetallic forming component metal, the amounts of Zn and Bi in the solder alloy

preferably is less than an amount which would produce a Bi:Sn atomic ratio of more than about 0.3 or Zn:Sn atomic ratio of more than about 0.3.

Similarly, in lead-free solder alloys where In is the predominant intermetallic forming component metal, the Zn:In atomic ratio preferably is less than about 0.3 and the Bi:In atomic ratio preferably is less than about 0.3; in lead-free solder alloys where Ga is the predominant component metal, the Zn:Ga atomic ratio preferably is less than about 0.3 and the Bi:Ga atomic ratio preferably is less than about 0.3.

Various optional additives may be combined with the high melting point additive to form an additive package. Examples of optional additives include but are not limited to antioxidants, metastable polymers, compounds which have affinity for oxygen, grain refiners which induce nucleation from the melt to give a finer scale microstructure with improved mechanical properties, dross control agents, inert fillers such as glass and minerals, and fluxes.

Antioxidants which may be employed include but are not limited to metals such as Si, Ti, Zr, Al, Nb, and Cr; metastable polymers which may be employed include but are not limited to those which have active carbon-oxygen-hydrogen groups such as carbonates and acetals; compounds which have affinity for oxygen which may be employed include but are not limited to boric acid and boron oxide, phosphates such as boron phosphide and phosphoric acid, and graphite; examples of useful grain refiners include but are not limited to transition metals such as Re, Ir, Cr, Mo, W, Ta, and Nb; and examples of dross control additives include but are not limited to strong oxide formers such as Si, Ca, Al, Ti, Zr, Nb, and Cr.

Fluxes also may be included in the additive package. Useful fluxes include but are not limited to active, water soluble, and inert fluxes. Examples of active fluxes include rosins, zinc chloride, ammonium chloride and other halide

salts, boric acid, borates and any other material that chemically reduces oxides or removes surface contamination on the substance to be soldered. Water soluble fluxes include fluxes which employ combinations of the above active flux ingredients chosen so that the flux is soluble in water and can be rinsed. Inert fluxes are non-chemically active fluxes, usually in polymer form, which produce a coating that prevents oxidation or degradation of the solder alloy and the substrate during soldering.

The additive package may be in the form of multiple core wires, twisted strands of wires, mixed powders, and laminated sheet preforms produced by techniques such as extrusion which are well known in the art.

The amounts and particle sizes of the lead-free solder alloy and high melting point additive metal, as well as optional additives can be varied over a wide range. The amounts and types of high melting point additives can be varied to control the rate of formation of a high melting point intermetallic compound based on the melting range of the lead-free solder alloy. In addition, the amount and type of optional additives can be varied to protect the lead-free solder alloy from oxidation during melting.

The amounts and types of lead-free solder alloy and high melting point additive metal may be varied to produce an intermetallic compound which has a desired remelt temperature and creep resistance at high temperatures such as are experienced during operation of lamps such as high intensity discharge lamps. Preferably, the amounts and types of high melting point additive metals are selected to react with the lead-free solder alloy to produce an intermetallic compound which has a solidus temperature above about 225°C, more preferably above about 250°C.

Preferably, the amounts and types of high melting point additive metals and lead-free solder alloy are chosen to produce an intermetallic compound that is about 80% or more

liquid at 350°C upon first melting. Preferably, the liquidus of the intermetallic compound formed from the composition after soldering and cooling is about 300°C to about 450°C.

The compositions of lead-free solder alloy and high melting point additive, as well as optional additives can be combined into various forms such as pastes, wires, strip, ribbon and rod.

In a paste, powders of the lead-free solder alloy and additives are combined with a viscous polymeric carrier, usually a flux. The amounts and sizes of particles of the lead-free solder alloy, high melting point additive, as well as optional additives can be chosen to produce a paste which has a desired rheological behavior, and viscosity, as well as shape retention after application to the substrate. Useful forms of wires include composite wires such as those which have a higher melting point additive in the form of a core such as a Cu core surrounded by a sheath of the lead-free solder alloy.

The high melting point intermetallic compounds are produced by reacting a mixture of lead-free solder alloy and a higher melting point additive metal. The lead-free solder alloy, when in its molten state, has solubility for the higher melting point additive metal. The mixture of lead-free solder alloy and additive metal has a melting point between 140°C and 250°C when first melted.

When molten lead-free solder is in contact with the high-melting additive, a transient liquid phase reaction occurs. During reaction of the molten, lead-free solder alloy and the high melting point additive metal, a transient liquid phase reaction occurs during first melting to produce a high melting point intermetallic compound. The transient liquid phase reaction occurs to produce an intermetallic compound which has a melting point of about 250°C or more. The transient liquid phase reaction enables formation of the intermetallic compound in-situ.

During the transient liquid phase reaction, a free low melting point metal such as Sn, In and Ga in the lead-free solder alloy reacts with a high melting point additive metal such as Cu, Fe, Ti and Ni to consume the free low melting point metal and to form a high melting point intermetallic compound. This reaction is described by equation I:

(I): free low melting point metal in lead-free solder alloy (molten) + high melting point additive (solid) → high melting point intermetallic compound(solid).

This transient liquid phase reaction can be used with a wide range of amounts and types of lead-free solder alloys and high melting point additive metals to form a variety of intermetallic compounds.

The intermetallic compounds can be produced have solidus and liquidus temperatures of from about 250°C to about 1490°C. For example, when a molten lead-free solder alloy which has free Sn reacts with a higher melting point additive metal such as Cu, the free Sn is consumed to produce a high melting point, Cu-Sn intermetallic compound such as Cu_6Sn_5 that is stable up to about 415°C. Formation of Cu_6Sn_5 can continue until all of the free Sn is consumed. Similarly, where the high melting point additive metal is Ti, the free Sn reacts with Ti to form Sn_5Ti_6 that is stable up to about 1494°C; where the high melting point additive metal is Ni, the free Sn reacts with Ni to form Ni_3Sn_4 that has a remelt temperature greater than about 790°C; where the high melting point additive metal is Fe, the free Sn reacts with Fe to form $FeSn_2$ that has a remelt temperature of about 513°C. Similarly, free Ga can react with Cu to form $CuGa_2$ that has a remelt temperature of about 254°C, and Ni can react with free In to form $Ni_{28}In_{72}$ that is stable to about 400°C.

The amount and type of high melting point additive metal employed can vary depending on the lead-free solder alloy. The amount of high melting point additive metal added to the lead-free solder alloy is sufficient to reduce the amount of a low melting point free metal such as free Sn to about 2 at.% to about 10 at.%, preferably about 6 at.% to about 8 at.%, based on the total atomic weight of the solder alloy and additive metal. To illustrate, during reaction of a lead-free solder alloy with a Cu high melting point additive as in Example 10 of Table 3, low melting point free Sn in the solder alloy reacts with the Cu additive to form a high melting point Cu_6Sn_5 intermetallic compound. In doing so, the amount of free Sn is reduced by 2 at.% per each 1 wt.% of Cu added, according to the rule of mixtures.

Examples 9-14:

Using the procedure above, high melting point intermetallic compounds are produced. Examples 9-14 of Table 3 show mixtures of lead-free solder alloy and high melting point additive metal for production of a high melting point intermetallic compound. In Table 3, preferred compositions are represented by examples 9-12.

Table 3
Mixture Used for Manufacture of Intermetallic Compounds

Example	**Solder Alloy**	**High Melting Point Additive Metal**
9	20Bi-33Sb-47Sn	0.5% Ti
10	5Cu-24Sb-71Sn	0.5% Ti
11	2Cu-25Ag-73Sn	0.5% Ti
12	1Cu-5Sb-94Sn	0.5% Ti
13	20Bi-33Sb-47Sn	2.0% Cu
14	20Bi-33Sb-47Sn	5.0% Cu

The amounts of the elemental metals in the mixtures used to make the intermetallic compounds of examples 9-14 are shown in Table 3A. In Table 3A, all amounts are in wt.%. based on the total weight of the mixture. These amounts are calculated by taking the elemental metals shown in the alloys used in the mixtures of Table 3 and applying the rule of mixtures to calculate the amounts of elemental metals present after addition of the Cu or Ti additive.

Table 3A
ELEMENTAL METALS EMPLOYED IN MIXTURES USED TO PRODUCE INTERMETALLIC COMPOUNDS

	Component Metal 1	Component Metal 2	Component Metal 3	Component Metal 4	Component Metal 5	Additive 1	Additive 2
Ex.	Wt.% Ag	Wt.% Bi	Wt.% Sb	Wt.% Sn	Wt.% Cu	Wt.% Ti	Wt.% Cu
9	0	42.8	24.9	31.8	0	0.5	0
10	0	0	27.9	59.7	11.9	0.5	0
11	25.9	0	0	57.7	15.9	0.5	0
12	0	0	10	87.5	2	0.5	0
13	0	42.1	24.5	31.4	0	0	2
14	0	40.9	23.8	30.4	0	0	5

Intermetallic compounds produced in examples 9-14 of Table 3 are analyzed by electron microprobe and inductively coupled plasma mass spectroscopy. The wt.% amounts of elemental metals in the lead-free solder alloys of examples 3,6,7 and 8 and the wt.% amounts of metals in the intermetallic compounds produced in examples 9-14 are shown in Table 4. In addition, the amounts of free tin in the lead-free solder alloys of examples 3,6,7 and 8 are shown.

In examples 9-14, the amounts of free tin in the lead-free solder alloys employed are expressed in at.% based on the total weight of the lead-free solder alloy and additive. The amount of free tin in the lead-free solder alloy for alloys which contain tin, bismuth, copper, titanium, antimony and silver is the total at.% tin minus any tin bound in intermetallics such Cu_6Sn_5, SbSn, Ag_3Sn and Ti_6Sn_5 present in the solder, or in the intermetallic compound from reaction of the solder and additive. The amount of free tin is calculated

from Equation II:

$$\text{II: At.\% Free Tin} = (\text{Total At.\% Sn} - 5/6\ (\text{at.\% Cu}) - 5/6\ (\text{at.\% Ti}) - (\text{at.\% Sb}) - 1/3\ (\text{at.\% Ag})$$

where each of the at.% Sn, at.% Cu, at.% Ti, at.% Sb, and at.% Ag are based on the total atomic percents of Sn, Cu, Ti, Sb and Ag in the mixture of solder alloy and high melting point additive. For other elements such as In and Ga, the amount of free In and Ga is calculated similarly by subtracting the atomic% of In and Ga bound into intermetallic phases such as CuGa and $Ni_{28}In_{72}$.

Table 4
Wt.% Elemental Metals in Solder Alloys and Intermetallic Compounds

	Metal 1	Metal 2	Metal 3	Metal 4	Metal 5	Additive 1	Additive 2		
Ex.	Wt.% Ag	Wt.% Bi	Wt.% Sb	Wt.% Sn	Wt.% Cu	Wt.% Cu	Wt.% Ti	At.% Free Sn	At. Ratio Bi:Sn
3	0	20	33	47	0	0	0	16.4	0.2
6	0	0	24	71	5	0	0	12.8	0
7	25	0	0	73	2	0	0	58.2	0
8	0	0	5	94	1	0	0	86.9	0
9	0	19.9	32.8	46.8	0	0	0.5	15.0	0.2
10	0	0	23.9	70.6	5	0	0.5	36.9	0
11	24.9	0	0	72.6	2	0	0.5	56.6	0
12	0	0	5	93.5	1	0	0.5	84.8	0
13	0	19.6	32.3	46.1	0	2	0	12.4	0.2
14	0	19	31.4	44.6	0	5	0	6.6	0.2

Solder Pastes

The lead-free solder alloys, as well as mixtures of the solder alloys with high melting point additives, can be used in solder pastes. Solder pastes include atomized powders of the lead-free solder alloys. Solder pastes also can include mixtures of these solder alloys and high melting point additives, together with optional additives such as antioxidants.

In manufacture of the solder pastes, powders of lead-free solder alloy, optionally with high melting point additives, are mixed with a flux, preferably in a 90/10 wt. ratio of powder to flux. This ratio may be varied to achieve desired rheological characteristics in the solder paste.

Lamp Fabrication and Evaluation

The lead-free solder alloys discussed in the first aspect of this invention, as well as mixtures of the solder alloy and high melting point additives, can be used in a variety of application such as high intensity discharge lamps, sealed beam lamps and composite lamps. A high intensity discharge lamp **1,** as shown in FIGS. 1 and 1A, includes outer envelope **3**, base **5**, eyelet **7**, lead wires **9** and **11,** and light source **13.** The lower section of outer envelope **3,** shown in FIG.1A, is threaded to join with matching threads on the inside of base **5**. This lower section of outer envelope **3** includes dimple **12** into which lead wire **9** is placed. In dimple **12,** wire **9** is joined to wall **4** of base **5** in a side solder joint.

Base **5** can be formed from a non-passivating transition metal such as Cu, brass, bronze, and Cu-based composite materials such as W-Cu, Ta-Cu, and Mo-Cu where the copper content is approximately 15 wt.% or more; Fe, mild steels, tool steels which have low chromium content; Ni, monel, and Ni-plated alloys; silver and sterling silver; Zn and high-Zn alloys such as Zn die-casting alloys; noble metals and alloys such as 10-24 karat gold, gold-plated alloys and platinum.

Base **5** also can be formed from a passivating alloy such as stainless steel, titanium and its alloys, zirconium and its alloys, as well as aluminum and its alloys depending on the choice of flux. Useful fluxes which may be used with passivating alloys include, alone or in combination, zinc chloride, ammonium chloride, hydrochloric acid, hydrofluoric acid, sodium hydroxide and any other chemical that can break

down the passive oxide layer on the surface of the alloy.

Outer envelope **3** can be formed from a broad range of glass compositions which can withstand the soldering temperatures. Useful glass compositions include but are not limited to:

1. borosilicates which have about 73% SiO_2, about 14.8% B_2O_3, about 5.45% PbO, about 3.6% Na_2O, and about 3.15%Al_2O_3;

2. borosilicates which have about 76.6% SiO_2, about 14.9% B_2O_3, about 2.4% Al_2O_3, about 4.4% Na_2O, about 0.6% K_2O, about 0.4% CaO, about 0.3% MgO, and about 0.4% Al_2O_3; and

3.borosilicates which have about 73.3% SiO_2, about 14.8% B_2O_3, about 5.45% PbO, about 3.6% Na_2O, about 2.05% Al_2O_3, about 0.4% K_2O, about 0.2% CeO_2, and about 0.2% trace impurities.

Lead wires **9, 11** can be Ni-plated Fe, and eyelet **7** can be formed from, such as, Cu/Zn 37% alloy. Ni-plated Fe and Cu/Zn37% alloys each are well known and commercially available.

Examples of a suitable light source **13** include but are not limited to an arc tube assembly, a sodium light assembly, a mercury vapor light assembly, a metal halide assembly, a ceramic metal halide assembly, and a tungsten filament.

Soldering of Components of High Intensity Discharge Lamp

First lead wire **9** is positioned in dimple **12** for contact with sidewall **4** of base **5**. Lead wire **11** is threaded through a hole in eyelet **7**. Base **5** then is placed onto envelope **3**. Solder paste which includes one of the afore described lead free solder alloys, or a mixture of one of these lead free solder alloys and high melting point additive, is applied to wire **9** at dimple **12**. The paste is heated to form a soldered side joint between sidewall **4** and wire **9**. Solder paste also is applied to wire **11** and eyelet **7** and heated to form a soldered eyelet joint with eyelet **7**.

In forming each of the soldered side joint and the soldered eyelet joint, the solder paste is heated to burn out the flux in the paste and to fully melt the solder to form the joint.

Cast wire soldering

To illustrate cast wire soldering, a side joint between wire **9** and sidewall **4** of base **5** formed of brass is made by using a wire solder formed from a lead-free solder alloy such as that of example 6 of Table 4.

Formation of the side joint is accomplished by preheating base **5**. A flux is applied to dimple **12** that has lead wire **9** therein and to side wall **4**. The wire solder is inserted into dimple **12**. Dimple **12** and sidewall **4** areas are then heated until the solder is molten and flows to produce the side joint. Similarly, solder wire is applied to wire **11** and eyelet **7** and heated to form a soldered eyelet joint with eyelet **7**.

Cast wire soldering likewise can be performed using composite wires formed of high melting point additives such as Cu, Cu alloy, Ti, Ni, Ni alloys, Pd, bronze, and brass encapsulated in a sheath of the lead-free solder alloy. Additional additives such as antioxidants, wetting agents and flux also can be incorporated.

High intensity discharge lamps which employ solder joints from alloys 1 to 8 are evaluated in two tests. In the first test, the lamps are aged in aging racks with the base up for 2000 hours. All of the joints formed with alloys 1 to 8 passed this test because none of the joints showed any signs of cracking or remelting. In a second test, the lamps are placed into an oven in both a base up and a base down orientation. The oven then is heated to 250 °C and maintained at 250 °C for 2000 hours. Joints formed with alloys 3, 6 and 7 passed the second test because none of those joints showed any signs of cracking or remelting. However, corrosion was noticed in the joint formed from alloy 8 and remelting was observed in joints

formed from alloys 1, 2, 4 and 5.

In a further embodiment of high intensity discharge lamp **1**, base **5** can be attached to envelope **3** by an adhesive such as phenolic resin or methyl phenyl silicone resin applied to the threads on any of envelope **3** or base **5**. In this embodiment, lead wire **9** can be extended over an edge of base **5** and soldered to the exterior of base **5.**

In yet another embodiment of high intensity discharge lamp **1**, as shown in FIGS. 2-2C, base **5A** may be a positioned at a right angle to light source **13A.** Base **5A** includes base cap **35**, lamp lead wire **37**, and base lead wire **39**. In this embodiment, lamp leads **37** are fed through base holes **41** as shown in FIG. 2B and soldered to base lead **39**.

Other lighting applications in which the solders and intermetallic alloys of the invention may be used include sealed beam lamps and composite lamps.

Sealed beam lamp **40** shown in FIGS. 3 and 3A can be used in vehicles such tractors, aircraft and automobiles. Sealed beam lamp **40** includes lens **42** formed from materials such as glass, reflector **42A** formed from materials such as glass, light source **46,** lead wires **48,** ferrule **50,** ferrule cavity **52,** and base contacts **54.** Sealed beam lamp **40** is made by placing any of the afore described lead free solder alloys and mixtures of those alloys with high melting point additives into ferrule cavity **52,** and heating to their liquidus. Lead wire **48** then is placed into the resulting liquid material and is cooled to form a solid solder joint. Clear lens **56** of glass or heat resistant plastic then can be attached to reflector **58** by flame sealing or adhesive. Base contacts **60** are then soldered to ferrule **50** with any of the aforedescribed lead free solder alloys and mixtures of those alloys with high melting point additives.

Composite lamp **90**, as shown in FIGS. 4-4B, includes light source **80**, base **82** formed of plastic or plastic-metal

composite, metal lead wires **83**, metal feed-throughs **85** molded into base **82**, and metal base connections **84**. Feed-throughs **85** and base connections **84** may be a single component. Lead wires **83** attached to light source **80**, are guided through feed-throughs **85**. Solder formed of any of the aforedescribed lead free solder alloys and mixtures of those alloys with high melting point additives is melted into feed-throughs **85** to make a soldered joint between lead wires **83** and base connections **84**. This soldered joint can function to provide electrical connection between light source 80 as well as to retain alignment of light source **80** and lead wires **83**.

Accordingly, the soldered joint may include a solder alloy such as 20Bi-33Sb-47Sn,5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn, and 1Cu-5Sb-94Sn. The solder joint also may include the reaction products of a solder alloy such as 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn with Ti in an amount of about 0.5% wherein the amount of Ti is based on the weight of the alloy; reaction products of 20Bi-33Sb-47Sn with Cu in an amount of about 2.0% wherein the amount of Cu is based on total weight of the solder alloy; the reaction product of a solder alloy of 20Bi-33Sb-47Sn with Cu in an amount of about 5.0% wherein the amount of Cu is based on total weight of the lead-free, solder alloy.

Accordingly, the solder joint may include a solder alloy such as 20Bi-33Sb-47Sn,5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn, and 1Cu-5Sb-94Sn. The solder joint also may include the reaction products of a solder alloy such as 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn with Ti in an amount of about 0.5% wherein the amount of Ti is based on the weight of the alloy; reaction products of 20Bi-33Sb-47Sn with Cu in an amount of about 2.0% wherein the amount of Cu is based on total weight of the solder alloy; the reaction product of a solder alloy of 20Bi-33Sb-47Sn with Cu in an amount of about 5.0% wherein the amount of Cu is based on total weight of the lead-free, solder alloy.

In yet another embodiment of the invention, an improved fluorescent lamp such as linear flourescent lamp **100** as shown in FIGS. 5 and 5A. Linear flourescent lamps, as is well known in the art, includes hollow prongs **102** an lead wires **104** joined to prongs **102** and to coil **106**. Lead wires **104** receive electrical energy from prongs **102** to energize coil **106** for activation of lamp **100**. In the improved lamp **100**, a solder joint between lead wires **104** and prongs **102** is made by of any of the afore described lead free solder alloys and mixtures of those alloys with high melting point additives.

Accordingly, the solder joint may include a solder alloy such as 20Bi-33Sb-47Sn,5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn, and 1Cu-5Sb-94Sn. The solder joint also may include the reaction products of a solder alloy such as 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn with Ti in an amount of about 0.5% wherein the amount of Ti is based on the weight of the alloy; reaction products of 20Bi-33Sb-47Sn with Cu in an amount of about 2.0% wherein the amount of Cu is based on total weight of the solder alloy; the reaction product of a solder alloy of 20Bi-33Sb-47Sn with Cu in an amount of about 5.0% wherein the amount of Cu is based on total weight of the lead-free, solder alloy.

Benefits

The lead-free solder alloys and the high melting point, intermetallic compounds of the invention form strong, heat resistant, electrically conductive bonds between base **5** and outer envelope **3**, as well as between lead wires and each of base **5** and eyelet **7**. The lead-free solder alloys and the intermetallic compounds of the invention form solder joints which have mechanical integrity up to about 240 °C. These solder joints have a liquidus temperature below about 1490 °C, preferably between 450 °C and a solidus above about 250°C. Liquidus temperatures below about 450°C advantageously enable rework of the solder joints, if necessary. Liquidus

temperatures below about 450°C also advantageously avoid generating unacceptable thermal stresses in the glass envelope-metal base assembly of the high intensity discharge lamp.

The lead-free solder alloys and the high melting point intermetallic compounds formed from reaction of the lead-free solder alloy and high melting point additive of the invention, as discussed above, are especially suited for use in lighting applications such as high intensity discharge lamps. Other lighting applications include sealed beam lamps and composite lamps.

In addition to lighting applications, the alloys and intermetallic compounds of the invention may be used in, for example, automotive radiators, industrial assembly and any other application where it is important that the solder joint maintain integrity up to about 450°C.

The lead free solders and high melting point intermetallic compounds of the invention have a low initial melting point of about 140°C to about 225°C, and a higher remelt temperature of about 250°C to about 450°C. The low initial melting point allows for simpler industrial assembly than a homogenous solder alloy which has a remelt temperature in the same range.

The solder pastes and wire solders produced from the lead-free solder alloys, as well as from mixtures thereof with high melting point additives may be employed to solder a variety of substrates. Examples of these substrates include Cu, brass, bronze, Cu-based composite materials such as Mo-Cu, Ta-Cu, and W-Cu, having Cu contents greater than about 15 wt.%; Fe, mild steels, tool steels with low chromium content; Ni, monel (Ni-Cu alloys), Ni-plated alloys; silver, sterling silver; Zn and high-Zn alloys such as Zn die-casting alloys; noble metals and alloys such as 10-24 karat gold, gold-plated alloys, and platinum, and palladium alloys (Paliney alloys).

The low diffusivity of the solders and intermetallic compounds inhibit long-term diffusion and attendant failure modes caused by solder penetration of the substrate, oxidation, formation of reactive products, and creep. In addition, the intermetallic compounds are resistant to thermal fatigue. The solders and intermetallic compounds of the invention, when used in manufacture of high intensity discharge lamps, provide a strong mechanical/metallurgical bond between each of base **5**, eyelet **7** and the outer envelope **3** components of the bulb, as well as an electrically conductive bond between the lead wires of the bulb and each of the side wall and eyelets of the base. The bond does not degrade due to high/low temperature cycling.

The invention enables use of lead free solder alloys as well as use of mixtures of lead free solders and high melting point additives to produce solders which have a desired remelt temperature. The properties of the lead-free solder alloys and intermetallic compounds formed from the reaction of these alloys with high melting point additives can be tailored to achieve a heat resistant solder joint based on desired assembly times, flow behavior, as well as long-term creep and substrate penetration resistance.

The lead-free solder alloys, as well as mixtures thereof with high melting point additives, can be employed with a wide variety of fluxes, including extremely aggressive fluxes. Examples of aggressive fluxes are compositions which include acidic or basic compounds such as HF and highly aggressive salts. Since the flux removes oxides present on the substrate, the choice of flux is a function of the metal used in the substrate. For metals such as aluminum which oxidize easily to form strong oxide layers, aggressive compounds such as HF or chloride fluxes can be used with the solders of the invention. In addition, the solder alloys of the invention do not require chloride compounds for wetting of non-passivating substrates. This avoids undesirable corrosive attack of the

metal by chlorine.

Claims:

1. A lead-free solder alloy consisting essentially of Sn, Bi and Sb wherein Sn is present in an amount of about 47 wt.%, Bi is present in an amount of about 20 wt.%, and Sb is present in an amount of about 33 wt.%, all amounts based on total weight of the alloy.

2. A lead-free solder alloy consisting essentially of Sn, Sb, and Cu wherein Sn is present in an amount of about 71 wt.%, Sb is present in an amount of about 24 wt.%, and Cu is present in an amount of about 5 wt.%, all amounts based on total weight of the alloy.

3. A lead-free solder alloy consisting essentially of Sn, Cu and Ag wherein Sn is present in an amount of about 73 wt.%, Cu is present in an amount of about 2 wt.%, and Ag is present in an amount of about 25 wt.%, all amounts based on total weight of the alloy.

4. A lead-free solder alloy consisting essentially of Sn, Sb and Cu wherein Sn is present in an amount of about 94 wt.%, Sb is present in an amount of about 5 wt.%, and Cu is present in an amount of about 1 wt.%, all amounts based on total weight of the alloy.

5. A high melting point intermetallic compound comprising a reaction product of 20Bi-33Sb-47Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy.

6. A high melting point intermetallic compound comprising a reaction product of 5Cu-24Sb-71Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy.

7. A high melting point intermetallic compound comprising a reaction product of 2Cu-25Ag-73Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy.

8. A high melting point intermetallic compound comprising a reaction product of 1Cu-5Sb-94Sn solder alloy and Ti in an amount of 0.5% based on weight of the solder alloy.

9. A high melting point intermetallic compound comprising a reaction product of 20Bi-33Sb-47Sn solder alloy and Cu in an amount of 2.0% based on weight of the solder alloy.

10. A high melting point intermetallic compound comprising a reaction product of 20Bi-33Sb-47Sn solder alloy and Cu in an amount of 5.0% based on weight of the solder alloy.

11. A method of manufacture of a high melting point intermetallic compound comprising reacting a lead-free solder alloy which includes a low melting point metal selected from the group consisting of Sn, Ga and In with an additive which has a melting point greater than the melting point of the lead-free solder alloy, wherein at least one of Sn, Ga and In is present in the lead free, solder alloy in a sufficient amount whereby about 15 at.% to about 50 at.% of the low melting point metal, based on total at.% of the lead-free, solder alloy and high melting point additive, can react with the additive.

12. The method of claim 11 wherein the lead-free solder alloy includes more than about 45 wt.% Sn based on total weight of the solder alloy.

13. The method of claim 12 wherein the lead-free alloy includes more than about 60 wt.% Sn based on total weight of the solder alloy.

14. The method of claim 11 wherein the lead-free alloy includes more than about 80 wt.% Sn based on total weight of the solder alloy.

15. A method of manufacture of a high melting point intermetallic compound which has a solidus temperature above about 225°C comprising,

reacting a lead-free solder alloy which includes one or more low melting point component metals selected from the group consisting of Sn, Ga and In with an additive which has a melting point greater than the melting point of the lead-free solder alloy, wherein at least one of Sn, Ga and In is present in the solder alloy in a sufficient amount whereby about 15 at.% to about 50 at.% of at least one of Sn, Ga and In is free for reaction with the additive, based on total at.% of the alloy and high melting point additive.

16. A method of manufacture of a high melting point intermetallic compound comprising,

reacting a lead-free solder alloy which a low melting point metal selected from the group consisting of Sn, Ga and In with an additive selected from the group consisting of Co, Ni, Pd, Fe, Cu, Ag, Ti, and Au, wherein any one of Sn, Ga and In is present in a sufficient amount whereby about 15 at.% to about 50 at.% of the low melting point metal is free for reaction with the additive, based on total at.% of the alloy and additive.

17. The method of claim 16 wherein the lead-free solder alloy includes more than about 45 wt.% Sn based on total weight of the lead-free solder alloy.

18. A method for manufacture of a high melting point intermetallic compound comprising,

reacting a mixture having a lead-free solder alloy

including a low melting point metal selected from the group of Sn, In and Ga and an additive which has a melting point higher than the melting point of the lead-free solder alloy to cause a transient liquid phase reaction between the low melting point metal and the additive to produce an intermetallic compound which has a melting point of about 250°C or more.

19. The method of claim 18 wherein the additive is selected from the group consisting of Cu, Fe, Ti and Ni.

20. The method of claim 19 wherein the lead-free solder alloy is selected from the group consisting of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn with an additive selected from the group consisting of Cu or Ti

21. A method for manufacture of a high melting point intermetallic compound comprising,

reacting a mixture of lead-free, 20Bi-33Sb-47Sn solder alloy and Ti in an amount of 0.5% based on total weight of the 20Bi-33Sb-47Sn solder alloy and Ti to cause a transient liquid phase reaction between Sn and Ti to produce an intermetallic compound including Sn and Ti which has a melting point of about 250°C or more.

22. A method for manufacture of a high melting point intermetallic compound comprising,

reacting a mixture of lead-free, 20Bi-33Sb-47Sn solder alloy and Ti in an amount of 0.5% based on total weight of the 20Bi-33Sb-47Sn solder alloy to cause a transient liquid phase reaction between Sn and Ti to produce an intermetallic compound including Sn and Ti which has a melting point of about 250°C or more.

23. A method for manufacture of a high melting point intermetallic compound comprising,

reacting a mixture of lead-free, 20Bi-33Sb-47Sn solder alloy and Cu in an amount of 5% based on total weight of the 20Bi-33Sb-47Sn solder alloy to cause a transient liquid phase reaction between Sn and Cu to produce an intermetallic compound including Sn and Cu which has a melting point of about 250°C or more.

24. A method for manufacture of a high melting point intermetallic compound comprising,

reacting a mixture of a lead-free solder alloy selected from the group consisting of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn and Ti in an amount of 0.5% based on total weight of the solder alloy to cause a transient liquid phase reaction to occur between Sn and Ti to produce an intermetallic compound including Sn and Ti which has a melting point of about 250°C or more.

25. A method for manufacture of a high melting point intermetallic compound comprising,

reacting a mixture of a lead-free, 20Bi-33Sb-47Sn solder alloy and Cu in an amount of 2.0% based on total weight of the 20Bi-33Sb-47Sn solder alloy to cause a transient liquid phase between Sn and Cu to produce an intermetallic compound including Sn and Cu which has a melting point of about 250°C and more.

26. A high intensity discharge lamp comprising a base **5**, an envelop **3**, a light source **13**, an eyelet **7**, lead wires **9,11**, a soldered side solder joint between lead wire **9** and base **5**, and a soldered eyelet joint between lead wire **11** and eyelet **7**, the improvement wherein the soldered side joint comprises a solder alloy selected from the group consisting of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn, and 1Cu-5Sb-94Sn.

27. A high intensity discharge lamp comprising an base **5**, a glass envelop **3**, lead wire **13**, eyelet **7**, lead wires **9,11**, a soldered side solder joint between lead wire **9** and base **5**, and a soldered eyelet joint between lead wire **11** and eyelet **7**, the improvement wherein the soldered side joint comprises an intermetallic compound which is a reaction product of a solder alloy selected from the group consisting of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn with Ti in an amount of about 0.5% wherein the amount of Ti is based on the weight of the alloy.

28. A high intensity discharge lamp comprising a base **5**, a glass envelop **3**, light source **13**, eyelet **7**, lead wires **9,11**, a soldered side solder joint between lead wire **9** and base **5**, and a soldered eyelet joint between lead wire **11** and eyelet **7**, the improvement wherein the soldered side joint comprises an intermetallic compound which is a reaction product of 20Bi-33Sb-47Sn with Cu in an amount of about 2.0% wherein the amount of Cu is based on total weight of the solder alloy.

29. A high intensity discharge lamp comprising a base **5**, an envelop **3**, a light source **13**, an eyelet **7**, lead wires **9,11**, a soldered side solder joint between lead wire **9** and base **5**, and a soldered eyelet joint between lead wire **11** and eyelet **7**, the improvement wherein the soldered side joint comprises an intermetallic compound which is a reaction product of a solder alloy of 20Bi-33Sb-47Sn with Cu in an amount of about 5.0% wherein the amount of Cu is based on total weight of the lead-free, solder alloy.

30. A high intensity discharge lamp comprising a base **5**, a glass envelop **3**, light source **13**, eyelet **7**, lead wires **9,11**, a soldered side solder joint between light source **9** and base **5**, and a soldered eyelet joint between lead wire **11** and eyelet **7**,

the improvement wherein the soldered eyelet joint comprises a lead-free, solder alloy selected from the group consisting of 20Bi-33Sb-47Sn, 5Cu-24Sb-71Sn, 2Cu-25Ag-73Sn and 1Cu-5Sb-94Sn.

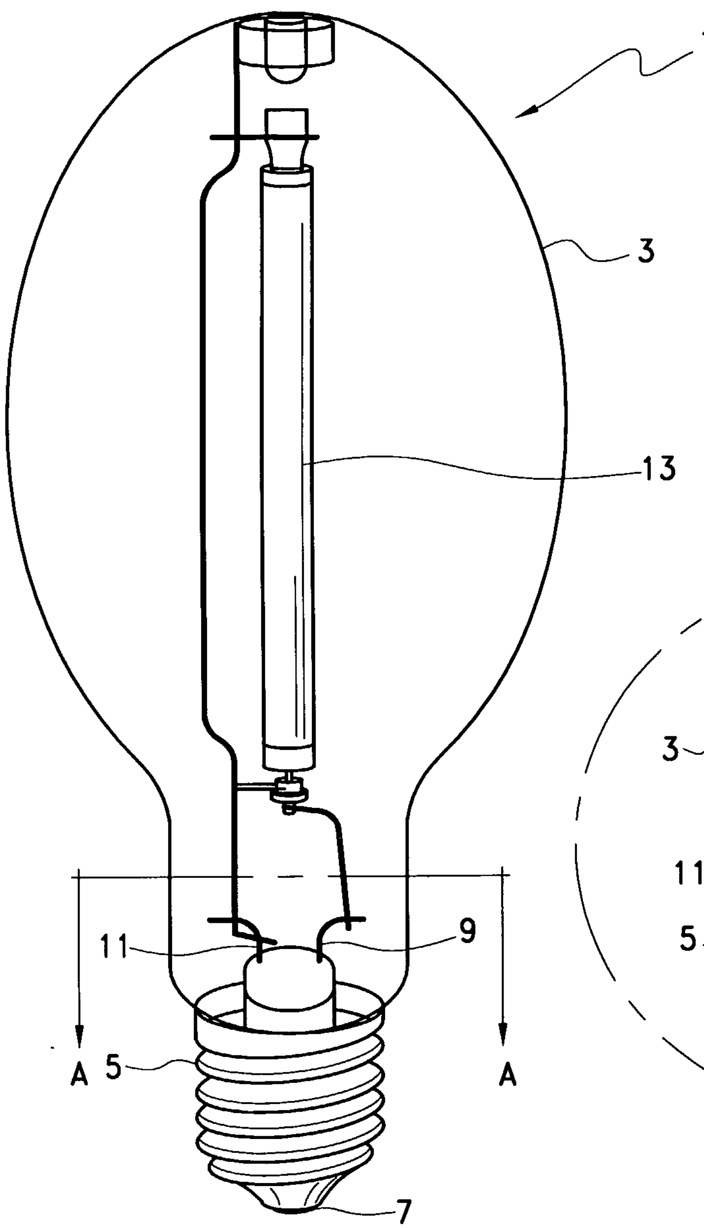

FIG.1

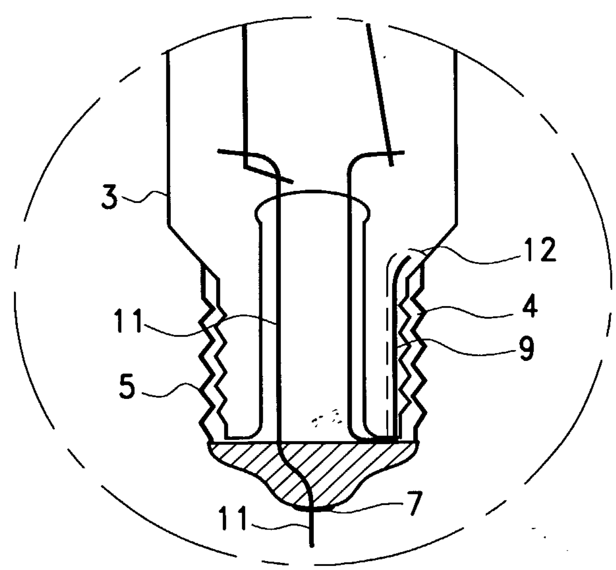

FIG.1A

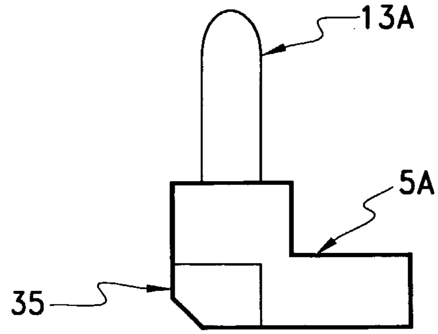

FIG.2

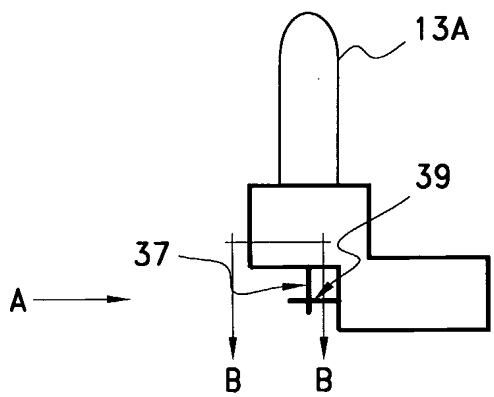

FIG.2A

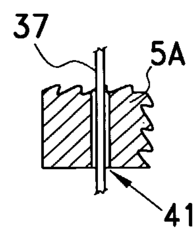

FIG.2B

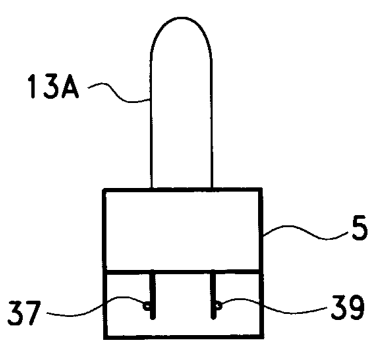

FIG.2C

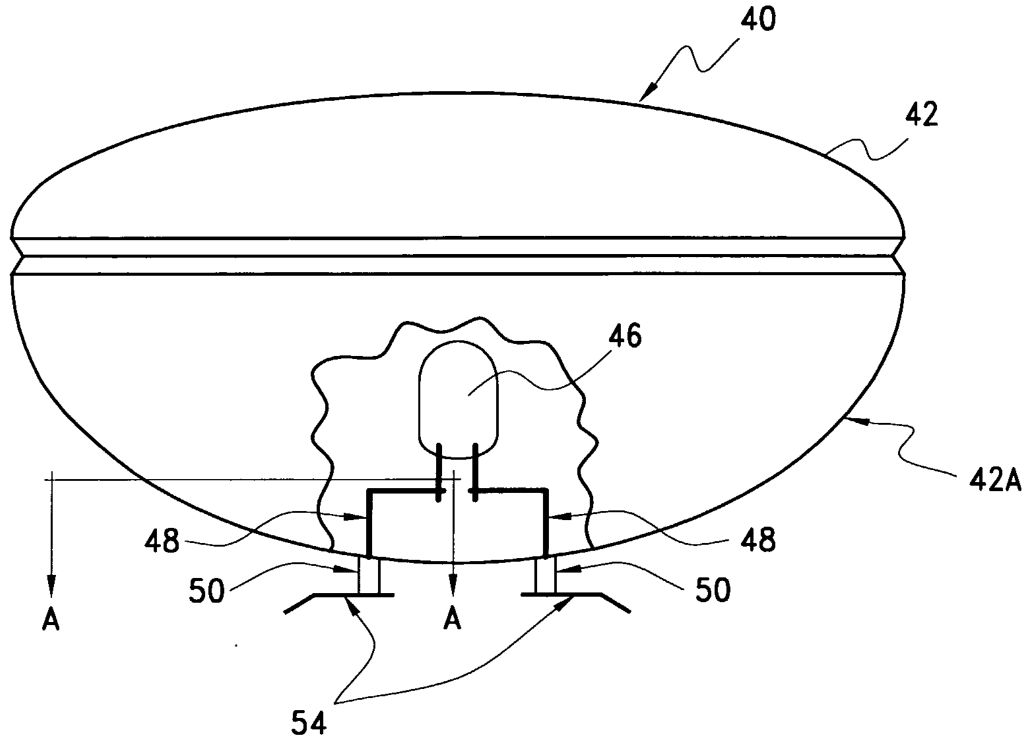

FIG.3

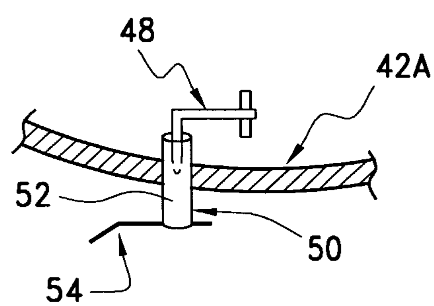

FIG.3A

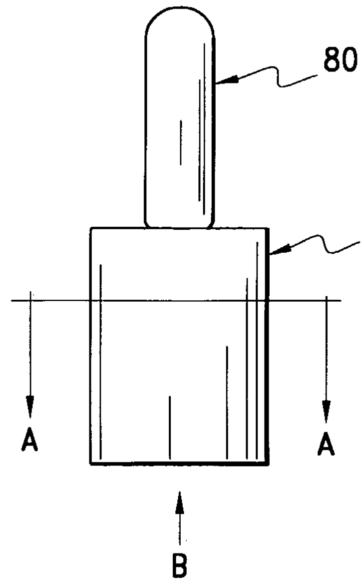

FIG.4

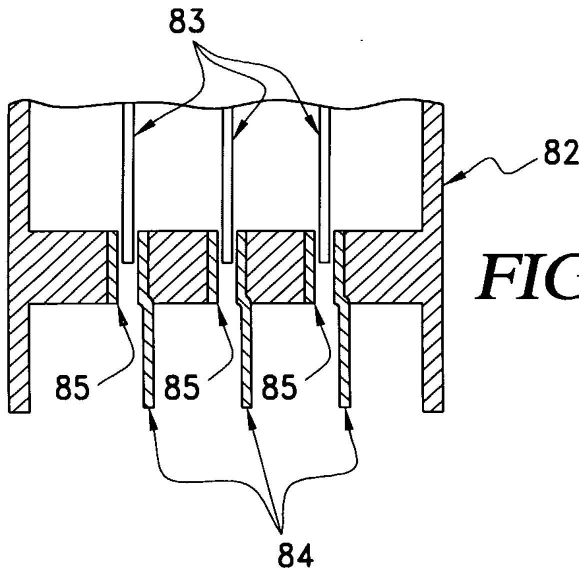

FIG.4A

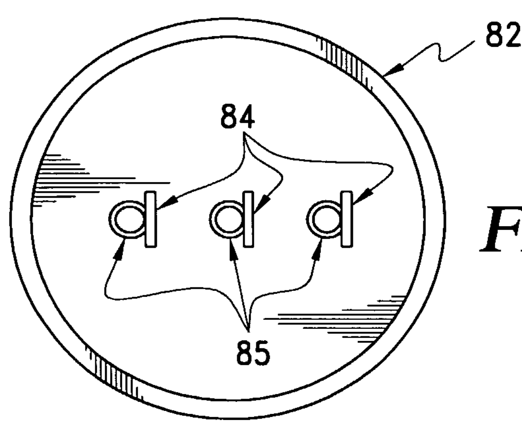

FIG.4B

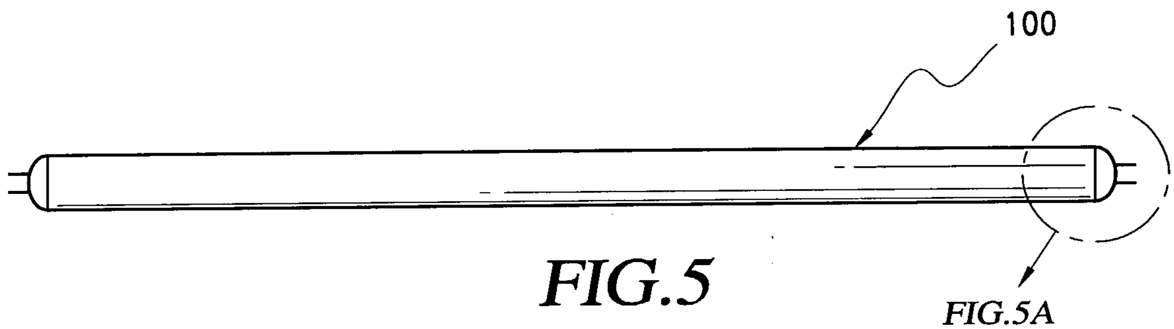

FIG.5

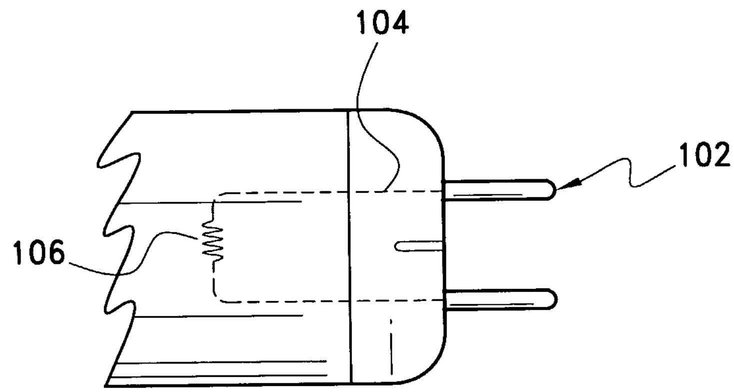

FIG.5A

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/28387

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : C22C13/00
US CL : 148/400, 442, 538; 420/560, 561, 562, 589 590; 313/25
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 148/400, 442, 538; 420/560, 561, 562, 589 590; 313/25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	Vecher, A.A.; Voronova, E. I.; Mechkovskii, L.A.;Skoropanov, A.S.,Determination of the enthalpies of mixing in gallium-indium-antimony and bismuth-tin-antimony systems by quantitative differential thermal analysis, Zh. Fiz. Khim. (1974), 48(4), 1007-9 (provided abstract only)	1 ----------- 5,11,12,15-30
Y	JP 06269982 A ((TOKURIKI HONTEN KK) 27 September 1994 (27.09.94), abstract.	11-30
Y	JP 06269983 A (TOKURIKI HONTEN KK) 27 September 1994 (27.09.94), abstract.	11-30
X --- Y	WO 2000048784 A (MULTICORE SOLDERS LIMITED) 24 August 2000 (24.08.00), abstract.	4 ----------- 8,11-30
Y	WO 9955924 A (ITRI LIMITED) 04 November 1991 (04.11.99) abstract.	1-30
X --- Y	US 4,667,871 A (MIZUHARA) 26 May 1987 (26.05.87), abstract.	3, 7 ----------- 11-30

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 February 2002 (09.02.2002)	27 MAR 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Sikyin Ip Telephone No. 703-308-0661

INTERNATIONAL SEARCH REPORT	International application No. PCT/US01/28387

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,550,422 A (SULCS et al) 27 August 1996 (27.08.96), figures 1-3 and col. 4, lines 64-67.	26-30

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/28387

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

Group I is, claim 1, drawn to a Pb-free solder alloy consisting essentially of 47Sn-20Bi-33Sb.
Group II is, claim 2, drawn to a Pb-free solder alloy consisting essentially of 71Sn-24Sb-5Cu.
Group III is, claim 3, drawn to a Pb-free solder alloy consisting essentially of 73Sn-2Cu-25Ag.
Group IV is, claim 4 drawn to a Pb-free solder alloy consisting essentially of 94Sn-5Sb-1Cu.
Group V is, claim 5, drawn to a high melting point intermetallic compound comprising a reaction product of 20Bi-33Sb-47Sn and Ti.
Group VI is, claim 6, drawn to a high melting point intermetallic compound comprising a reaction product of 5Cu-24Sb-71Sn and Ti.
Group VII is, claim 7, drawn to a high melting point intermetallic compound comprising a reaction product of 2Cu-25Ag-73Sn and Ti.
Group VIII is, calim 8, drawn to a high melting point intermetallic compound comprising a reaction product of 1Cu-5Sb-94Sn and Ti.
Group IX is, claim 9, drawn to a high melting point intermetallic compound comprising a reaction product of 20Bi-33Sb-47Sn and 2Cu.
Group X is, claim 10, drawn to a high melting point intermetallic compund comprising a reaction product of 20Bi-33Sb-47Sn and 5Cu.
Group XI is, claims 11-25, drawn to a method of manufacture of high melting point intermetallic compound including Sn, Ga, In and high melting point additives.
Group XII is, claims 26 and 30, drawn to a high intensity lamp comprising at least one solder selected from Groups I-IV above.
Group XIII is, claim 27, drawn to a high intensity discharge lamp comprising an intermetallic compound product of solder and Ti.
Group XIV is, claim 28, drawn to a high intensity discharge lamp comprising solder forms intermetallic compound with 2Cu.
Group XV is, claim 29, drawn to a high intensity discharge lamp comprising solder forms intermetallic compound with 5Cu.
The inventions listed as Groups I-XV do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reason: Each group contains different solder alloy composition and/or additives in different wt.%.

Continuation of B. FIELDS SEARCHED Item 3:

CA, EAST
Terms: tin, Sn, copper, Cu, silver, Ag, bismuth, Bi, antimony, Sb, HID, intensity, lamp, solder

DERWENT-ACC-NO: 2003-129574

DERWENT-WEEK: 200452

TITLE: Lead-free solder alloy used for high intensity discharge lamp, comprises essentially of preset amounts of tin, bismuth and antimony

INVENTOR: BOLLINA R; CAMPBELL L G ; GERMAN R M ; IACOCCA R G

PATENT-ASSIGNEE: PENN STATE RES FOUND[PENNN]

PRIORITY-DATA: 2001US-295883P (June 5, 2001)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 02099146 A1	December 12, 2002	EN
AU 2001290767 A1	December 16, 2002	EN

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI S K SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU MC MW MZ NL OA PT SD SE SL SZ TR TZ UG ZW

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO2002099146A1	N/A	2001WO-US28387	September 11, 2001
AU2001290767A1	Based on	2001AU-290767	September 11, 2001

INT-CL-CURRENT:

TYPE	IPC DATE
CIPS	B23K35/26 20060101
CIPS	C22C1/04 20060101
CIPS	C22C13/00 20060101
CIPS	C22C13/02 20060101
CIPS	H01J9/24 20060101

ABSTRACTED-PUB-NO: WO 02099146 A1

BASIC-ABSTRACT:

NOVELTY - A lead-free solder alloy comprises essentially of 47 wt.% of tin, 20 wt.% of bismuth and 33 wt.% of antimony.

DESCRIPTION - INDEPENDENT CLAIMS are also included for the following:

(1) a high melting point intermetallic compound;

(2) the manufacture of the high melting point intermetallic compound; and

(3) a high intensity discharge lamp (1).

USE - Used for a high intensity discharge lamps (claimed) including sealed beam lamps and composite lamps, and used in automotive radiators, industrial assemblies and other application where solder joint maintain integrity up to 450 degrees C.

ADVANTAGE - Solder joints formed from lead-free solder alloys are resistant to creep in high-temperature environments. The lead-free solder alloys and intermetallic compounds formed by reaction of lead-free, solder alloy and high melting point additive metal, have excellent electrical conductivity, resistance to long term failure by creep, oxidation, and thermal fatigue, are able to sustain modest stresses in use and during installation, and can be easily repaired. The lead-free solder alloys and high melting point, intermetallic compounds form strong, heat resistant, electrically conductive bonds between base and outer envelopes as well as between lead wires and each of base and eyelet. The lead-free solder alloys and high melting point, intermetallic compounds form solder joints which have mechanical integrity up to 240 degrees C, liquidus temperature below 1490 degrees C, preferably below 450 degrees C and solidus temperature above 250 degrees C. Liquidus temperature below 450 degrees C enables rework of the solder joints if necessary, and avoid generating unacceptable thermal stresses in the glass envelope-metal base assembly of discharge lamp. The lead-free solder alloys and high melting point, intermetallic compounds have a low initial melting point of 140-225 degrees C and a higher remelt temperature of 250-450 degrees C. The low initial melting point allows for simpler industrial assembly. The low diffusivity of the solders and intermetallic compounds inhibit long term diffusion and attendant failure modes caused by solder penetration of the substrate, oxidation, formation of reactive products and creep. The solder alloys do not require chlorine compounds for wetting of non-passivating substrates. This avoids undesirable corrosive attack of the metal by chlorine.

DESCRIPTION OF DRAWING(S) - The figure shows the front view of the high intensity discharge lamp.

High intensity discharge lamp (1)

CHOSEN-DRAWING:	Dwg.1/5
TITLE-TERMS:	LEAD FREE SOLDER ALLOY HIGH INTENSITY DISCHARGE LAMP COMPRISE ESSENTIAL PRESET AMOUNT TIN BISMUTH ANTIMONY

DERWENT-CLASS: L03 M26 X26

CPI-CODES: L03-C02; L03-H05; M26-B05; M26-B05A; M26-B05B;

EPI-CODES: X26-A01D; X26-A02X;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers:	2003-033295
Non-CPI Secondary Accession Numbers:	2003-102847